



Compatibility of Ti_3SiC_2 with liquid Pb and PbBi containing oxygen

A. Heinzl*, G. Müller, A. Weisenburger

Forschungszentrum Karlsruhe GmbH, Institute for Pulsed Power and Microwave Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany

A B S T R A C T

Ti_3SiC_2 is considered as a possible pump material for heavy liquid metal (HLM) cooled nuclear systems because it resists oxygen and has high temperature strength. Therefore the material was tested in stagnant lead and lead bismuth containing oxygen at temperatures between 550 and 750 °C up to 4000 h in the Karlsruhe COSTA facilities. Two different oxygen concentrations (10^{-6} and 10^{-8} wt%) were chosen. During the exposure a thin TiO_x -layer was formed at the surface of the specimens. No dissolution attack was observed under these conditions.

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1. Introduction

Liquid lead and lead bismuth have been considered as coolants for future accelerator driven systems (ADS) and lead cooled fast reactors (LFR). In the proposed designs the pumps are placed in the hot temperature region of the reactor [1]. This combines corrosion attacks at elevated temperature and erosion expected at the impeller and the body of the pump. In the recent design of the industrial scale ADS called EFIT (European Facility for Industrial Transmutation) temperatures of around 480 °C and flow velocities of 10 m/s at the pump are expected [2].

In general, the countermeasure against liquid metal corrosion, which means dissolution of structural components by liquid lead alloys, is the formation of a protective oxide scale on the metal surface which is stabilized by oxygen dissolved in the liquid alloy [3]. The oxide scale hinders cation diffusion from the steel or other material into the liquid metal and anion diffusion in the opposite direction. This method was extensively studied and described recently [4]. It was shown that martensitic steels like T91, without surface protection, form thick oxide layers consisting of magnetite and spinel in which magnetite tends to spall off above temperatures of 500 °C. Also, even flow velocities of 2 m/s influence the corrosion behavior [5]. The magnetite scale disappears because it is instantly removed. Therefore, materials with good corrosion resistance to both liquid Pb/PbBi and oxygen are required. Recently, corrosion experiments in oxygen containing stagnant lead with steels used in conventional pumps and SiSiC composite material were reported [6]. It was shown that the composite material has the best behavior. Another composite material, the machinable ceramic Ti_3SiC_2 is also considered for use in lead alloys. Good behavior in oxygen reduced lead at 650 and 800 °C was recently reported [7].

The aim of this work is to study the behavior of Ti_3SiC_2 in Pb and Pb-55.5Bi with 10^{-6} and 10^{-8} wt% oxygen at temperatures between 550 and 750 °C up to an exposure time of 4000 h.

2. Experimental section

2.1. Material

Ti_3SiC_2 (MAXTHAL® 312) supplied by KANTHAL was selected for the corrosion tests. The material is one of the $M_{n+1}AX_n$ phase family, where M is titanium, A denotes either aluminium or silicon and X is carbon. Ti_3SiC_2 is produced by hot isostatic pressing of mixed Ti, SiC and C powders. It is a ternary ceramic which combines metallic and ceramic properties. It has a high thermal strength, high melting point and high chemical resistance typical of ceramics. Its service temperature in air is limited to 1000 °C [8–10]. Like a metal, Ti_3SiC_2 resists thermal shock and has excellent electrical and thermal conductivity. Also, it is creep as well as fatigue resistant and readily machinable. Unfortunately, it cannot be welded and, compared with binary carbide ceramics like WC and TiC, it is relatively soft and not wear resistant [10].

The test specimens with dimensions $28 \times 8 \times 2 \text{ mm}^3$ were cut out of a supplied bar. The X-ray diffraction (XRD) measurement of an as fabricated specimen showed that the delivered material consists of Ti_3SiC_2 with small amounts of unreacted TiC_x , Fig. 1(a). (The other patterns will be discussed later. They refer to material condition after the test.) Fig. 2 shows a cross-section through the as received Ti_3SiC_2 . There are pores in the size range 1–2 μm to 20–30 μm . The dark grey grains are unreacted TiC_x .

2.2. Test facility (COSTA) and test conditions

The corrosion tests were carried out in the COSTA (corrosion test stand for stagnant liquid alloys) facility [11]. The COSTA device consists of a furnace with a quartz tube as a reaction tube in which

* Corresponding author. Tel.: +49 7247 82 8447; fax: +49 7247 82 2256.
E-mail address: Annette.heinzl@ihm.fzk.de (A. Heinzl).

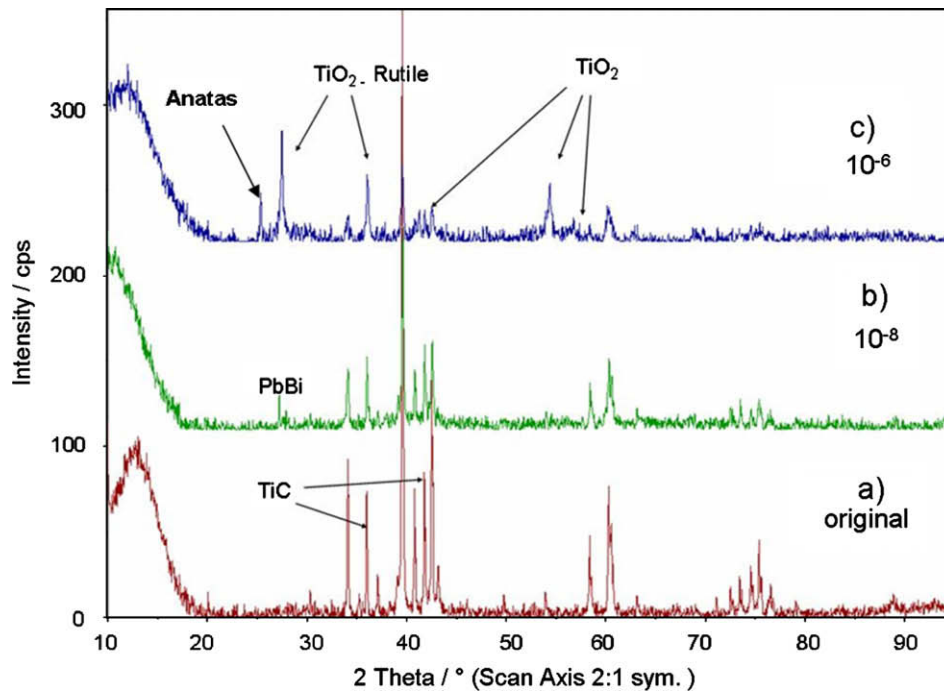


Fig. 1. XRD spectra of as delivered Ti_3SiC_2 (a) and Ti_3SiC_2 samples which were exposed to PbBi containing 10^{-6} (b) and 10^{-8} wt% (c) oxygen for 3000 h at 650 °C.

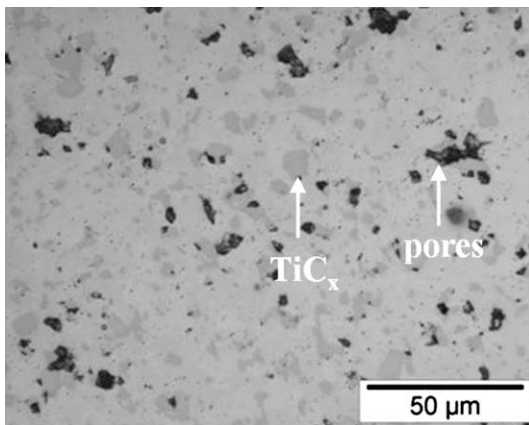


Fig. 2. Cross-section of as delivered Ti_3SiC_2 with pores in the range of some few μm up to 20–30 μm . Dark grey grains are unreacted TiC_x .

the samples hang inside Pb/PbBi filled crucibles. The oxygen concentration in the liquid metal is controlled via the gas atmosphere. The oxygen partial pressure in the gas atmosphere, which is established by a defined $\text{H}_2/\text{H}_2\text{O}$ ratio, determines the chemical potential of oxygen in the liquid metal [12]. The test conditions are listed in Table 1. Ti_3SiC_2 was tested in liquid Pb containing 10^{-6} or 10^{-8} wt% oxygen between 550 and 750 °C for times up to 4000 h. The specimens in liquid PbBi were tested at oxygen concentrations of 10^{-6} and 10^{-8} wt% up to 3000 h at 550 and 650 °C.

2.3. Analysis

After extracting the specimens from the COSTA facility they were cut with a diamond disk saw perpendicular to the exposed surface. One part of the sample was embedded, ground and polished for metallographic examinations. A light optical (LOM) and a scanning electron (SEM) microscope (S-800, Hitachi) with an energy dispersive X-ray analysis system (EDX, WINEDS Thomson

Table 1

Test conditions.

| Medium | Temperature (°C) | Oxygen concentration (wt%) | Exposure time (h) |
|--------|------------------|----------------------------|-------------------|
| Pb | 550 | 10^{-6} | 4000 |
| | | 10^{-8} | 4000 |
| | 600 | 10^{-6} | 4000 |
| | | 10^{-8} | 4000 |
| | 750 | 10^{-6} | 500, 2000 |
| PbBi | 550 | 10^{-6} | 3000 |
| | | 10^{-8} | 3000 |
| | 650 | 10^{-6} | 3000 |
| | | 10^{-8} | 3000 |

Scientific) were used for the analysis. To identify crystallographic phases on the surface of the Ti_3SiC_2 using XRD (Rich Seifert XRD 3003), the second part of the specimen was cleaned of the adherent PbBi using cooking oil. The oil was then removed by acetone.

3. Results

The surfaces of all specimens exposed to Pb or PbBi containing 10^{-6} and 10^{-8} wt% oxygen are oxidized. Fig. 3(a) shows the cross-section of the Ti_3SiC_2 specimen exposed for 4000 h in liquid Pb with an oxygen concentration of 10^{-6} wt% at 550 °C. The bright zone at the top is adherent Pb. The surface of the specimen is covered by a thin ($\leq 1 \mu\text{m}$) oxide scale (dark band) with some internal oxidation extending to 6 μm . The scale consists only of titanium oxide. Above this oxide scale there is a titanium oxide layer which contains Pb. The presence of Pb in this area can have different reasons, e.g., Pb contamination in the scale during preparation or most probably Pb inclusions penetrated during the oxide layer formation.

With increasing temperature, the oxide scale thickness increases as well. Fig. 3(b) shows the cross-section of Ti_3SiC_2 after 2000 h at 750 °C in liquid Pb containing 10^{-6} wt% oxygen. In this case a non-homogenous thick oxide layer of approximately 7 μm

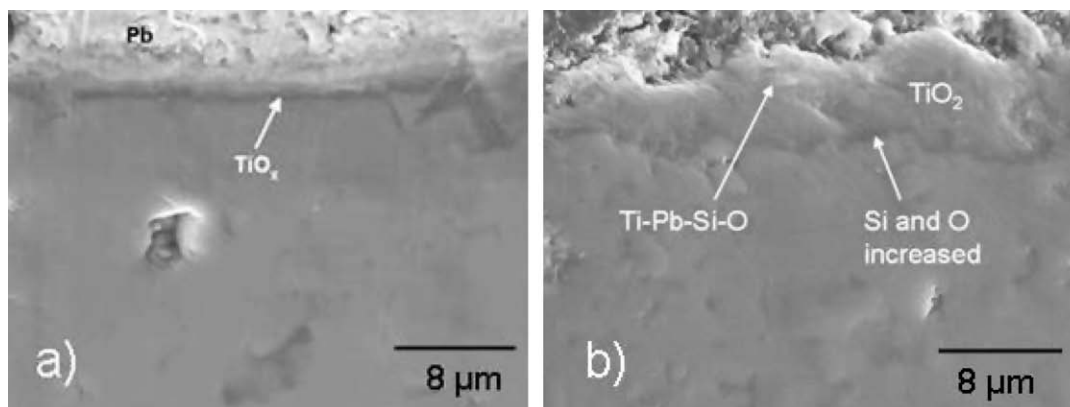


Fig. 3. Cross-section of Ti_3SiC_2 exposed to Pb containing 10^{-6} wt% oxygen for 4000 h at 550°C (a) and 2000 h at 750°C (b). Both surfaces are covered by a TiO_2 layer which contains Pb inclusions or a compound of Ti–Pb–Si–O close to the surface.

covers the surface. Bright spots appeared in the outer oxide layer consisting of Ti–Si–Pb–O detected by EDX. Underneath, a nearly pure TiO_2 scale was formed. The slightly darker line observed in Fig. 3(b) at the oxide bulk interface indicates an increase in oxygen and silicon content.

The specimen exposed to Pb with 10^{-6} wt% oxygen at 650°C is also covered by a continuous oxide layer with some internal oxidation, Fig. 4(a). Fig. 4(c) shows the oxidized surface of the sample which was cleaned of PbBi by hot oil. The surface of the oxide is very rough. XRD analysis detected the existence of the thin oxide scale, Fig. 1(c). The pattern shows a rutile phase with only a small anatase peak as well as the strongest Ti_3SiC_2 peaks. Pb or PbBi inclusions were not detected.

At the lower oxygen concentration of 10^{-8} wt% in Pb and PbBi the main behavior of the specimens did not change. A very thin

titanium oxide scale was formed on the surface at all temperatures. Fig. 4(b) and (d) shows the specimen exposed for 3000 h at 650°C in PbBi containing 10^{-8} wt% oxygen. Fig. 4(b) is the cross-section of the specimen. The oxide layer is too thin to be visible, but it was confirmed by EDX measurements on the surface. The dark visible layer on the surface is embedding material. A photo of the surface is shown in Fig. 4(d). The oxide here is thinner and smoother than at 10^{-6} wt%. It is so thin that no peaks appear in the XRD spectra of Fig. 1(b).

4. Discussion

All specimen developed thin oxide layers on the surface in contact with Pb and PbBi containing 10^{-6} and 10^{-8} wt% oxygen. The

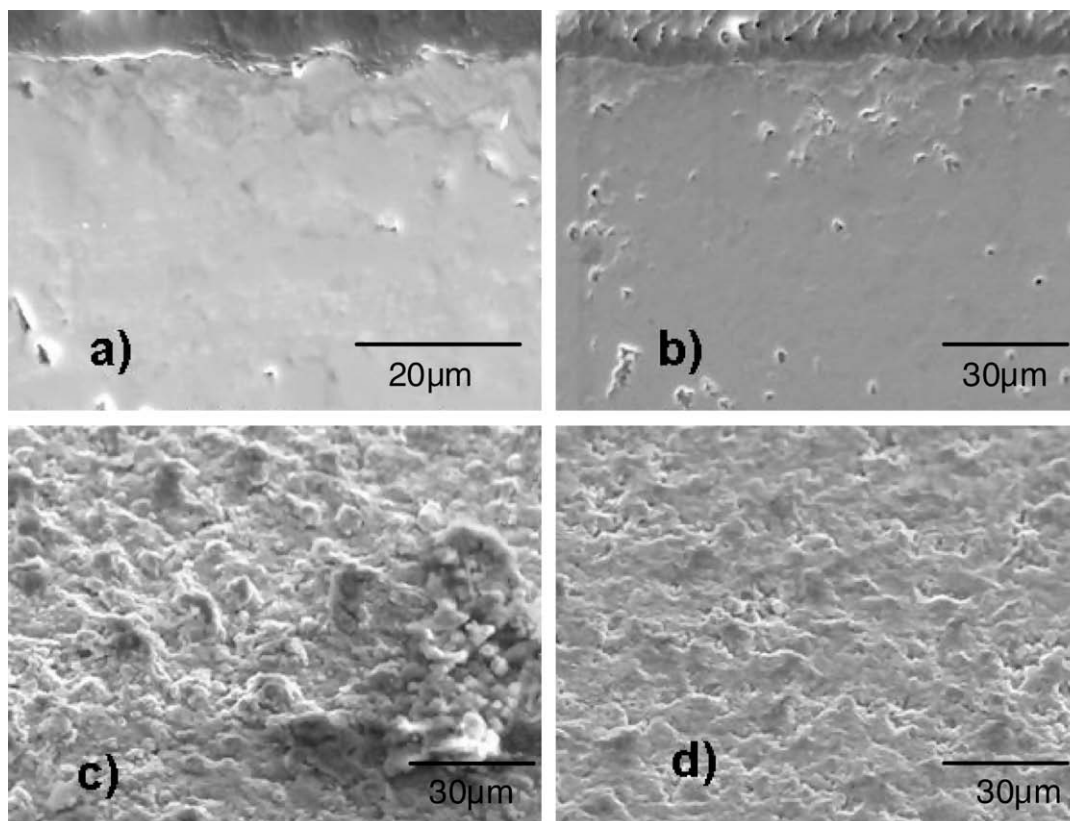


Fig. 4. Cross-section and photos of the samples surface of Ti_3SiC_2 exposed to PbBi containing 10^{-6} wt% (a and c) and 10^{-8} wt% (b and d) oxygen for 3000 h at 650°C .

thickness is around 1 μm at low temperatures after 4000 h and thicker (around 7 μm) at 750 °C after only 2000 h.

There is one examination of Ti_2SiC_3 in liquid Pb reported in literature [7]. Only a small reaction zone was observed after 1000 h in Pb at 650 °C with an oxygen concentration much lower than in our experiments. Calculation of the oxygen concentration in lead [12] using the $\text{H}_2/\text{H}_2\text{O}$ ration of about 5×10^3 in the experiment yields a oxygen concentration of 10^{-12} wt% that, however, is still high enough to form SiO_2 and TiO_2 . Unfortunately the reaction zone is not defined in this paper, but it must be assumed that an oxide scale prevents dissolution attack on the Ti_2SiC_3 surface. This agrees with the result of our tests at 10^{-6} and 10^{-8} wt% oxygen at 550 and 650 °C and 4000 h duration. The corrosion process is restricted to oxide formation at the surface. These oxide scales are slowly growing and acceptable at least for temperatures below 650 °C and an exposure of 4000 h.

Compared to experiments conducted in air [9,10,13,14] layers observed are much thinner and exhibit a zone enriched in Si only after the test at 750 °C. However, the EDX analysis does not clearly reveal a stratified layer like observed in the above literature, which refers mostly to experiments at temperatures above 800 °C. It is not yet clear if the low temperature alone or also the low oxygen potential provided by the oxygen dissolved in Pb and PbBi is responsible for this difference. It should be noted that even at 650 °C the greater part of titanium oxide consists of rutile, as shown in the XRD pattern of Fig. 1(c). However, there is a hint in literature [15,16] that rutile exists at temperatures as low as 500 °C if the oxygen partial pressure is 0.6 Pa or lower.

5. Summary and conclusions

All specimens showed the formation of an oxide scale on the surface when exposed to liquid Pb and PbBi containing 10^{-6} and 10^{-8} wt% oxygen. No dissolution attack was observed at 550 to

750 °C which leads to the assumption that Ti_3SiC_2 can be used in Pb and PbBi under these conditions at least up to 4000 h. The oxide scale consists mainly of TiO_2 in the rutile phase. The formation of an outer rutile layer agrees with descriptions of the oxidation behavior of Ti_3SiC_2 at high temperatures in air [9,10] and with Ti oxidation at low oxygen partial pressures [13,14]. An inner layer consisting of amorphous SiO_2 and fine crystalline TiO_2 , observed in the high temperature experiments, could not be confirmed. The erosion stability of this material will be investigated in fast flowing Pb and PbBi (up to 20 m/s) in the future.

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